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<b>(21) International Application Number:</b> PCT/BE93/00065 <b>(22) International Filing Date:</b> 15 October 1993 (15.10.93) <b>(71) Applicant (for JP only):</b> FINA RESEARCH S.A. [BE/BE]; Zone Industrielle C, B-7181 Seneffe (BE). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> DEBRAS, Guy [BE/BE]; Rue de la Chapelle 12, B-6210 Les Bons Villers (BE). <b>(74) Common Representative:</b> FINA RESEARCH S.A.; Patent Dept., Zone Industrielle C, B-7181 Seneffe (BE).		<b>(81) Designated States:</b> JP, US.  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PROCESS FOR PRODUCING POLYETHYLENE HAVING A BROAD MOLECULAR WEIGHT DISTRIBUTION  <b>(57) Abstract</b>  A process for the homo- or co-polymerization of ethylene in two liquid full loop reactors in series wherein the average molecular mass is regulated with hydrogen, characterised by the introduction of the comonomer (if any) in the first reactor, and by very low and very high hydrogen concentration respectively in the first and second reactor.		

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PROCESS FOR PRODUCING POLYETHYLENE HAVING  
A BROAD MOLECULAR WEIGHT DISTRIBUTION

The present invention concerns a process for producing polyethylene having a broad molecular weight distribution. More particularly, the present invention relates to the production of high density polyethylene having a broad or bimodal molecular weight distribution.

For high density polyethylene, hereinafter referred to as polyethylene, the molecular weight distribution (MWD) is one of the basic properties that determines the properties of the polymer, and thus its end-uses.

Although it may be difficult to evaluate the influence of each property taken independently, it is generally accepted that the molecular weight mostly determines the mechanical properties while the molecular weight dispersion mostly determines the rheological properties.

There is a demand for high molecular weight polyethylene, because an increase of the molecular weight normally improves the physical properties of the resins. However, high molecular weights tend to make polymers harder to process. On the other hand, an increase in the MWD tends to improve the flowability at high shear rate during the processing. Thus, broadening the MWD is one way to improve the processing of high molecular weight (= low melt flow index) polyethylene, in applications requiring fast processing at fairly high die swell, such as in blowing and extrusion techniques.

Some believe that, in polyethylene having a high molecular weight combined with a broad MWD, the lower molecular weight portion aids in processing while the higher molecular weight portion contributes to the good impact resistance of the film, such polyethylene can be processed at higher throughput rate with lower energy requirements.

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The MWD may be described completely by the curve obtained by gel permeation chromatography. However, a good evaluation, also called the polydispersity index, is represented by the ratio of the weight average to the number average molecular weight.

Depending on the applications, the required MWD will range from 10 to 30.

It was first proposed to prepare polyethylene having broad MWD by blending polyethylenes having different molecular weights in order to obtain the advantages of a broad distribution, however, the results were not satisfactory.

It has also been proposed to use several reactors connected in series.

For this purpose a process is known for the preparation of polymodal ethylene polymer in which ethylene is polymerized in two stages in the presence of a halogen-containing organoaluminum compound, a transition metal compound and different amounts of hydrogen in each stage (GB 1233599).

A process is furthermore known for the preparation of olefin polymers by a two-stage polymerization, a highmolecular polymer being prepared in the first stage at a low  $H_2/C_2H_4$  ratio and a low-molecular polymer being prepared in the second stage at high  $H_2/C_2H_4$  ratio (EP-A 57,352). The catalyst used is, inter alia, a halogen-containing organoaluminum compound together with the reaction product of an oxygen-containing organomagnesium compound and an oxygen-containing organotitanium compound, both of which are in solution, and an aluminum halide.

Both known processes give polyolefins with a good processability and good physical properties. Film produced from these polyolefins shows only few fish eyes.

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It has also been proposed a process to polymerize ethylene in two stages according to which the pressure in the second reactor is kept lower than in the first one; the polymerization is carried out in the presence of usual Ziegler-Natta catalyst such as a transition metal catalyst supported on a solid carrier and an organoaluminum compound. Examples of such processes are described in US patents 4,414,369 and 4,338,424.

However, the ethylene polymers obtained with such process are not very convenient as regard to their mechanical properties.

It is therefore an object of the present invention to provide a process to polymerize ethylene to form ethylene polymers with good processability, good physical properties and diverse applicability and which are easy to carry out.

It has been found that this object can be achieved with a two-stage process involving specific operating conditions, that is liquid full loop reactors.

#### SUMMARY OF THE INVENTION

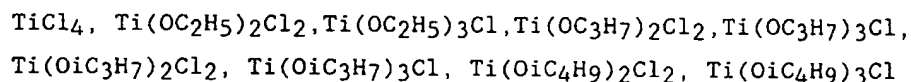
It has now been found that polyalkenes with a wide molecular weight distribution and a very good homogeneity can be obtained by the process of polymerizing ethylene, optionally with at most 20 mole % of one or more other alpha-alkene of 3 to 10 carbon atoms, in two liquid full loop reactors in series at a temperature of 50 to 120°C, preferably 60 to 110°C under an absolute pressure of 1 to 100 bar in the presence of a catalyst consisting of a transition metal component (component A) which is the reaction product of an organomagnesium compound with a titanium compound and an organoaluminum compound (compound B), the average molecular mass being regulated with hydrogen,

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which process comprises carrying out the polymerization such that the introduction of a co-monomer if any is carried out essentially in the first reactor and that the hydrogen concentration is at a very low concentration in the first reactor to form ethylene polymers having HLMI between 0.01 and 5g/10', while maintaining a very high hydrogen pressure in the second reactor to form ethylene polymers having a HLMI higher than 5g/10'.

As transition metal compounds suitable for the preparation of component A, there are used tetravalent halogenated titanium compounds, preferably titanium compounds of the general formula  $TiX_n(OR)_{4-n}$  in which n is 1 to 4, X stands for chlorine or bromine, and R for identical or different hydrocarbon radicals, especially straight-chain or branched alkyl groups having 1 to 18, preferably 1 to 10, carbon atoms.

Examples thereof are:



In some cases, it may be advantageous to prepare the halogeno-ortho-titanic acid esters of the above formula in situ by reacting the respective ortho-titanic acid ester with  $TiCl_4$  in a corresponding proportion.

This reaction is advantageously carried out at temperatures of from 0 to 200° C., the upper temperature limit being determined by the decomposition temperature of the tetravalent halogenated titanium compound used; it is advantageously carried out at temperatures of from 60 to 120° C.

The reaction may be effected in inert diluents, for example aliphatic or cycloaliphatic hydrocarbons as are currently used for the low pressure process such as butane, pentane, hexane, heptane, cyclohexane, methyl-cyclohexane as well as aromatic hydrocarbons, such as benzene or toluene; hydrogenated Diesel oil fractions which have been carefully freed from oxygen, sulfur compounds and moisture are also useful.

Subsequently, the reaction product of magnesium alcoholate and tetravalent halogenated titanium compound which is insoluble in hydrocarbons is freed from unreacted titanium compound by washing it several times with one of the above inert diluents in which the titanium-(IV)-compound used is readily soluble.

For preparing component A, magnesium alcoholates, preferably those of the general formula  $Mg(OR)_2$  are used, in which R stands for identical or different hydrocarbon radicals, preferably straight-chain or branched alkyl groups having 1 to 10 carbon atoms; magnesium alcoholates having alkyl groups of from 1 to 4 carbon atoms are preferred. Examples thereof are  $Mg(OCH_3)_2$ ,  $Mg(OC_2H_5)_2$ ,  $Mg(OC_3H_7)_2$ ,  $Mg(OiC_3H_7)_2$ ,  $Mg(OC_4H_9)_2$ ,  $Mg(OiC_4H_9)_2$ ,  $Mg(OCH_2-CH_2-C_6H_5)_2$ .

The magnesium alcoholates can be prepared by known methods, for example by reacting magnesium with alcohols, especially monohydric aliphatic alcohols.

Magnesium alcoholates of the general formula  $X-Mg-OR$  in which X stands for halogen,  $(SO_4)_{1/2}$  carboxylate, especially acetate or OH, and R has the above meaning, may also be used.

These compounds are, for example, obtained by reacting alcoholic solutions of the corresponding anhydrous acids with magnesium.

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The titanium content of component A may be within the range of from 0.05 to 10mg.-atom, per gram of component A. It can be controlled by the reaction time, the reaction temperature and the concentration of the tetravalent halogenated titanium compound used.

The concentration of the titanium component fixed on the magnesium compound is advantageously in the range of from 0.005 to 1.5 mmol, preferably from 0.03 to 0.8mmol, per litre of dispersing agent or reactor volume. Generally, even higher concentrations are possible.

The organo-aluminum compounds used may be reaction products of aluminum-trialkyl or aluminum-dialkyl hydrides with hydrocarbon radicals having 1 to 16 carbon atoms, preferably  $\text{Al}(\text{iBu})_3$  or  $\text{Al}(\text{iBu})_2\text{H}$  and diolefins containing 4 to 20 carbon atoms, preferably isoprene; for example aluminum isoprenyl.

Furthermore, suitable as component B are chlorinated organo-aluminum compounds, for example dialkyl-aluminum monochlorides of the formula  $\text{R}_2\text{AlCl}$  or alkyl-aluminum sesquichlorides of the formula  $\text{R}_3\text{Al}_2\text{Cl}_3$ , in which formulae R stands for identical or different hydrocarbon radicals, preferably alkyl groups having 1 to 16 carbon atoms, preferably 2 to 12 carbon atoms, for example  $(\text{C}_2\text{H}_5)_2\text{AlCl}$ ,  $(\text{iC}_4\text{H}_9)_2\text{AlCl}$ ,  $(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3$ .

It is advantageous to use, as component B, aluminum-trialkyls of the formula  $\text{AlR}_3$  or aluminum-dialkyl hydrides of the formula  $\text{AlR}_2\text{H}$ , in which formulae R stands for identical or different hydrocarbons, preferably alkyl groups having 1 to 16, preferably 2 to 6, carbon atoms, for example  $\text{Al}(\text{C}_2\text{H}_5)_3$ ,  $\text{Al}(\text{C}_2\text{H}_5)_2\text{H}$ ,  $\text{Al}(\text{C}_3\text{H}_7)_3$ ,  $\text{Al}(\text{C}_3\text{H}_7)_2\text{H}$ ,  $\text{Al}(\text{iC}_4\text{H}_9)_3$ , or  $\text{Al}(\text{iC}_4\text{H}_9)_2\text{H}$ .

The organoaluminum may be used in a concentration of from 0,5 to 10 mmol per litre of reactor volume.



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The polymerization of ethylene is carried out slurry in two liquid full loop reactors connected in series.

As already indicated, it has been found that it is essential to introduce the alpha-olefin comonomer in the first reactor.

As comonomer which may be used in the present process, alpha-olefin having from 3 to 10 carbon may be cited, and preferably 1-hexene is used.

Ethylene is injected with the comonomer in the first loop reactor together the precontacted catalyst. Optionally the catalyst may comprise an usual electron-donor such as isoalkylphthalate.

The polymerisation is carried out at a temperature of from 50 to 120°C, preferably from 60 to 110°C at a pressure of 1 to 100 bar, and preferably 30 to 50 bar.

The residence time in the first reactor, may be shorter or larger than in the second reactor, depending on the HMW/LMW ratio desired for the end polymer. The hydrogen is maintained at a low concentration comprised between 0.005-0.07 vol% in the first reactor and between 0.5-2.2 vol% in the second reactor.

The ethylene polymer stream obtained in the first reactor is transferred in the second loop reactor. The polymerization is pursued at a pressure comprised between 30 and 50 bar; at a temperature between 50 and 100°C and preferably between 80 and 110°C. The residence time is generally comprised between 0.5 and 1 hour.

Under the polymerization conditions, it has been found that the high molecular weight part of the polymer is formed in the first reactor. Generally, this part represents from 10 to 90% and preferable 30 to 70wt% of the bimodal polymer.

One of the feature of the present invention resides in the fact that the ethylene, catalyst and comonomer are injected in the first reactor leads to better mechanical properties.

The following examples are given to illustrate the process of the invention without limiting its scope.

Examples 1 to 6

The polymerization of ethylene was carried out in two liquid full loop reactors connected in series, in accordance with the polymerization process described hereabove, under the conditions specified in table 1.

Isobutane (35 gk/h) is used as diluant. Tibal concentration is given with regard to  $iC_4$  amount.

Physical and mechanical (flexural modulus, ESCR) properties for the final product are also summarized in table 1.

Comparative example 7

The polymerization of ethylene was carried out in a single reactor under reaction conditions indicated in table 1. The properties of the monomodal resin obtained are also described in the same table.

We obtain a better ESCR-Flexural Modulus compromise with the bimodal resins.

TABLE 1

Examples	1	2	3	4	5	6	7
<b>1st reactor</b>							
Temp. (°C)	75	75	70	71	71	75	90
Tibal (ppm)	350	350	350	350	350	350	525
C2- (kg/h)	3	2.5	4	3.9	4	4	8.4
C6- (cc/h)	230	300	250	250	150	150	270
H2 (Nl/h)	2.1	1.2	10	10	10.5	10.5	60
Resid.time (min)	70	70	70	70	70	70	60
<b>2nd reactor</b>							
Temp. (C°)	95	95	95	95	95	95	
Tibal (ppm)	350	350	350	350	350	350	
C2- (kg/h)	5	5.5	4	4	4	4	
H2 (Nl/h)	300	150	300	300	300	250	
Resid.time (min)	35	35	35	35	35	35	
<b>OFF GAS</b>							
C2- (wt%)	4.6	4.7	4.5	4.4	4.6	4.3	4.3
C6- (wt%)	0.17	0.21	0.27	0.22	0.13	0.14	0.34
H2 (vol%)	1.9	0.9	1.8	1.9	1.94	1.6	0.33
<b>Product from 1st reactor</b>							
HIMI (g/10')	0.29	0.22	0.77	1.67	1.42	2.4	
Density (g/cc)	0.933	0.925	0.942	0.940	0.944	0.946	
HMW Part(w%)	+/-50	+/-40	+/-60	+/-60	+/-60	+/-60	
<b>Final product</b>							
HIMI (g/10')	14.8	17.1	13.3	22.5	15.9	18.9	11
MI2 (g/10')	0.09	0.17	0.1	0.2	0.15	0.17	0.19
Density (g/cc)	0.952	0.950	0.952	0.954	0.953	0.955	0.952
Mn (kDa)	13	17	15.9	14.4	13.9	15.1	26
Mw (kDa)	230	206	238	208	208	195	173
Mz (kDa)	1837	1525	1899	1780	1622	1480	1027
MWD	17.2	12.1	15.0	14.8	14.9	12.9	6.7
<b>FLEXURAL MODULUS</b>							
at 0.4% (mPA)	1520	1480	1570	1490	1520	1520	1420
<b>ESCR</b>							
Bell 50°C 100%(h)	Fo>300	Fo>300	186	140	150	130	53

## CLAIMS

1. Process for polymerizing ethylene, optionally with at most 20 mole % of one or more other alpha-alkene of 3 to 10 carbon atoms, in two liquid full loop reactors in series at a temperature of 50 to 120°C, preferably 60 to 110°C under an absolute pressure of 1 to 100 bar in the presence of a catalyst consisting of a transition metal component (component A) which is the reaction product of an organomagnesium compound with a titanium compound, an organoaluminium compound (component B), and optionally one or more electron donor, the average molecular mass being regulated with hydrogen, which process comprises carrying out the polymerization such that the introduction of a co-monomer if any is carried out essentially in the first reactor, that the hydrogen concentration is at a very low concentration in the first reactor to form ethylene polymers having HLMi between 0.01 and 5g/10', and that a very high hydrogen pressure is maintained in the second reactor to form ethylene polymers having a HLMi higher than 5g/10'.
2. The process of claim 1, wherein the hydrogen concentration is of 0.005 to 0.07 vol % in the first reactor and of 0.5 - 2.2 vol % in the second reactor.
3. The process of claim 1, wherein the residence time in the first reactor is adjusted to produce 30 to 70 vol % of the total polymer.

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F10/02 C08F2/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 057 420 (SUMITOMO CHEMICAL COMPANY) 11 August 1982 see claims 1-3,5,8,9,12 see page 1, line 1 - page 4, line 19 see page 5, line 1 - line 10 see page 6, line 6 - line 19 see page 13, line 1 - line 3 see page 14, line 7 - line 16 see page 16, line 6 - line 10 see page 20; example 1 see page 24; example 2 see page 43; example 4 ---	1
A	EP,A,0 274 536 (MITSUI PETROCHEMICAL INDUSTRIES) 20 July 1988 see claims 1-3 see example 1 ---	1

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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

13 June 1994

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,92 12181 (NESTE OY) 23 July 1992 see claims 1-4 see page 5, line 20 - line 25 -----	1

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/BE 93/00065

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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